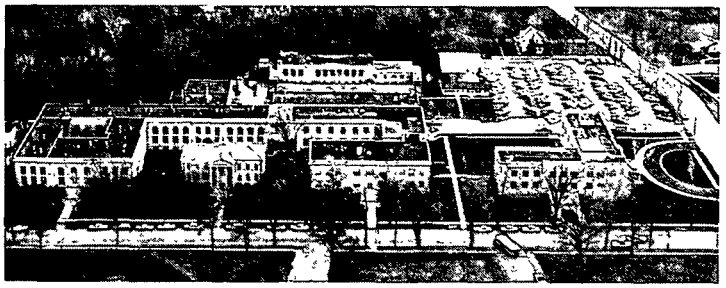

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A KINETIC STUDY OF KRAFT CHAR GASIFICATION WITH CO_2

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INTRODUCTION

Part of the burning of kraft black liquor in a recovery furnace is accomplished through a gasification reaction with carbon dioxide. This reaction occurs in a molten salt environment. Due to the high temperature, heterogeneity, and corrosive nature of the material in the char bed, knowledge of the gasification reactions occurring in the kraft recovery furnace is incomplete. Knowledge of the rate of black liquor char gasification will lead to a better understanding of the processes occurring in the char bed.

In this paper, the results of a kinetic study of carbon oxidation with carbon dioxide are presented. The objectives of this study are to determine the controlling parameters for this reaction and develop a rate expression that can be used to determine the relative importance of this reaction.

Although a considerable amount of data has been obtained for this gasification reaction with other forms of carbon, there is little information available for the reaction with kraft char. Because of the high inorganic content of the kraft char, the kinetics of this reaction may be different than the kinetics for other forms of carbon.

PREVIOUS RESEARCH

Many mechanistic studies of the carbon-carbon dioxide reaction have been reported, which give rise to a variety of rate equations. The simplest mathematical model for a gas-solid reaction was developed by Langmuir. The expression is

$$\text{Rate} = \frac{k_1 C}{1 + k_2 C} \qquad (1)$$

C = local gas concentration

Carbon gasification with CO_2 is believed to occur through the adsorption of CO_2 at an active site on the carbon surface, and by desorption of CO. Both adsorption and desorption can occur via a single site or dual site mechanism. This active site theory presumes a surface coverage less than a complete monomolecular layer (1). The Langmuir expression, however, is not adequate for large variations in temperature and pressure.

Ergun et al. (1) and Yamouchi and Mukaibo (2) reported a rate equation of

$$\text{Rate} = \frac{k_1 [CO_2]}{1 + k_2 [CO_2] + k_3 [CO]} \qquad (2)$$

which is the most widely accepted form. This adequately describes the CO_2 action and the CO inhibition for the overall reaction over ideal carbon surfaces.

Temkin et al. (2) claimed that the overall rate of reaction with CO_2 can be expressed by the equation

$$\text{Rate} = k_1 \left[\frac{[CO_2]}{1 + k_2 [CO]} \right]^{1/2} \quad (3)$$

In contrast to this equation, Blackwood (2) found that when nuclear-grade graphite was gasified in CO_2 at temperatures between 650 and 870 C and pressures from 1 to 30 atm, the results could be represented by the equation

$$\text{Rate} = \frac{k_1 [CO_2]}{1 + k_2 [CO]} \quad (4)$$

Coal chars that were produced at low temperatures, when gasified under similar conditions, give a very high rate of reaction. For these chars, an equation of the type

$$\text{Rate} = \frac{k_1 [CO_2] + k_4 [CO_2]^2}{1 + k_2 [CO] + k_3 [CO_2]} \quad (5)$$

was suggested by Blackwood and Ingeme (1,2).

Hedden and Lowe (2) gasified nuclear graphite in CO_2 at a partial pressure of 0.1-1.0 atm and found that Eq. (2) held only when the CO/CO_2 ratio was greater than 0.5; otherwise, the results were fitted better by the equation

$$\text{Rate} = \frac{k_1 [CO_2]}{1 + k_2 [CO]^{1/2} + k_3 [CO_2]} \quad (6)$$

Although activation energies for different forms of carbon vary, most authors (1,2) have obtained activation energies between 80 and 90 kcal/mole. Many workers have used carbons of unknown purity and obtained low activation energies because of these impurities. The activation energy for impure carbons is an average of 25 kcal/mole lower than for pure carbons. In kraft char, these impurities are inorganic salts.

The influence of different forms of mass transfer resistance on the gasification of char was studied by Li and van Heiningen (3). A heterogeneous system of black liquor char contained in a reactor vessel was used in their experiments. It was found that external mass transfer resistance is negligible in the gasification of char by carbon dioxide. The external mass transfer resistance was determined to be only 4-10% of the total mass transfer resistance.

EXPERIMENTAL SYSTEM

The experimental system used to study kraft char gasification with carbon dioxide is shown in Figure 1. To contain the molten sodium carbonate and char, ceramic alumina crucibles (4.13×10^{-2} m diameter, 1.05×10^{-1} m height) were used. The crucible was contained in a stainless steel retort, which was placed inside the heating coils of an induction furnace. Figure 2 is a schematic of the crucible-retort-coil design.

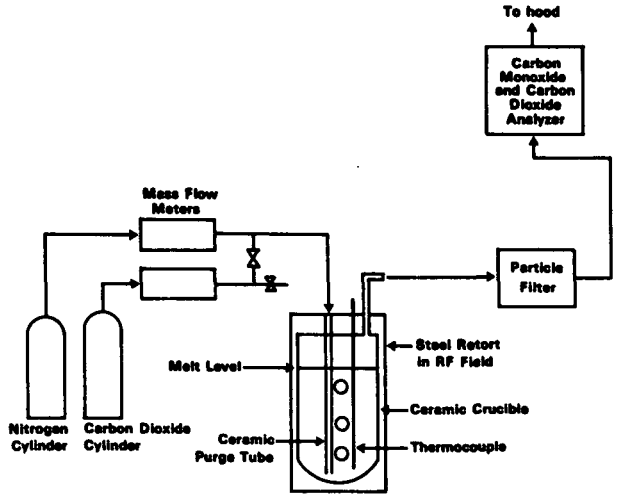

Figure 1. Schematic of experimental system used to study carbon dioxide oxidation of kraft char.

To measure the volumetric flow rate of nitrogen to the reactor, nitrogen was metered from a pressurized gas cylinder through a dry gas meter. A mercury manometer connected to the purge line served as a safety valve. The carbon dioxide was obtained and metered in the same manner. The carbon dioxide entered the nitrogen purge line before reaching the reactor to insure mixing of the two streams. The gases then flowed into the crucible by means of a 4.8×10^{-3} M inside diameter ceramic purge tube, which extended into the molten salts and caused mixing of the reactants. The open end of the purge tube was located as close to the bottom of the crucible as possible to try to obtain the most mixing. The temperature was monitored using a nickel-chromium vs. nickel-aluminum thermocouple.

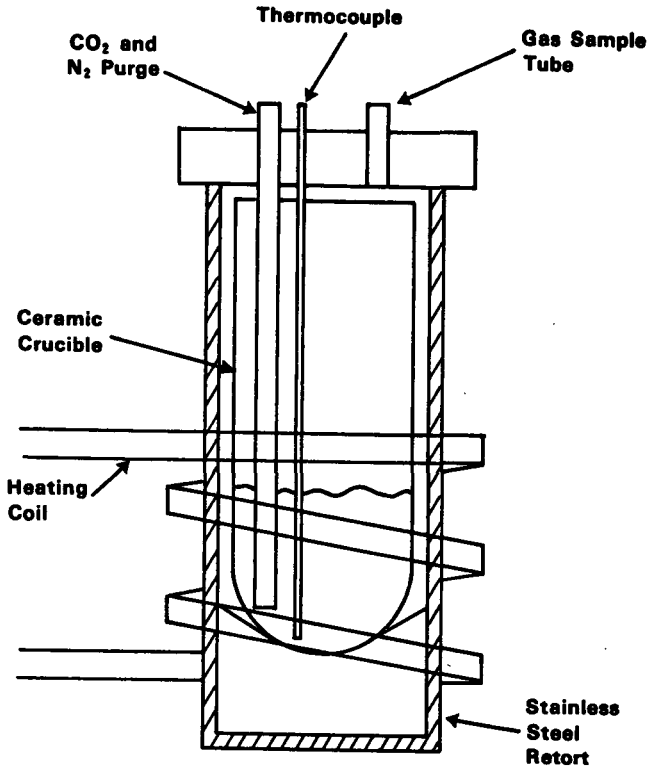

Figure 2. Experimental reactor used to study kraft char oxidation with carbon dioxide.

The gasification rate of reaction was followed by measuring the evolution of CO which was removed from the reactor (along with the N_2 and excess CO_2) through a 4.8 x 10^{-3}M inner diameter steel tube. These gases were passed through an infrared gas analyzer which was capable of simultaneously measuring the carbon dioxide level and carbon monoxide level in the off-gases. The analyzer was calibrated using a standard nitrogen, carbon monoxide, carbon dioxide mixture before each run and checked for drift afterward. The off-gases were vented to the hood after being analyzed for CO and CO_2 composition.

EXPERIMENTAL PROCEDURE

In most gasification runs, 0.77 mole anhydrous granular sodium carbonate and 0.024 mole carbon (1.0 g char at 28.8% carbon) were used. These reactants were mixed before being placed into the crucible.

The crucible, contained in the induction furnace, was slowly brought to the reaction temperature. During this heat-up period, nitrogen was continually purged through the system. The nitrogen flow rate was kept low enough to prevent the char from flying out of the crucible.

After the crucible temperature was stabilized at the reaction temperature, the nitrogen purge rate was increased. Once the system was stabilized with this new flow rate, the carbon dioxide was introduced into the system. The run was continued until the reaction rate no longer was rapidly decreasing or had leveled off.

EXPERIMENTAL RESULTS

Determination of Char Content

The organic content of the char was determined by reacting one gram of char with air. The organic carbon was defined as the carbon present in the char that is not in the form of carbonate. All the organic carbon was assumed to be converted into CO or CO_2, and the reaction was considered to be complete when the CO and CO_2 content of the off-gas dropped to zero. The carbon content of the char was found to be 28.8 ± 0.9%

Before proceeding to the gasification runs, the char was finely ground. The size distribution of this char was:

Particle Size, μm	% by Weight Greater Than
125	52.7
60	70.6
45	76.6
30	87.9
20	93.1
0	100.0

The stoichiometric equation describing the gasification of kraft char by CO_2 is

$$C + CO_2 = 2CO$$

Two moles of carbon monoxide are generated for every mole of carbon oxidized.

The char/molten salt mixture was considered to be in equilibrium with the gases above the melt during gasification. Therefore, when analyzing the data with respect to the partial pressure of CO_2 and CO, the concentration of the gases in the product stream was used as the concentration of these gases during reaction.

Effect of Carbon Concentration

To determine the effect of carbon concentration on carbon dioxide oxidation of char, the initial carbon concentration was varied. An increase in the amount of initial carbon produced an increase in the reaction rate. The effect of carbon concentration on the rate of gasification is shown in Figure 3.

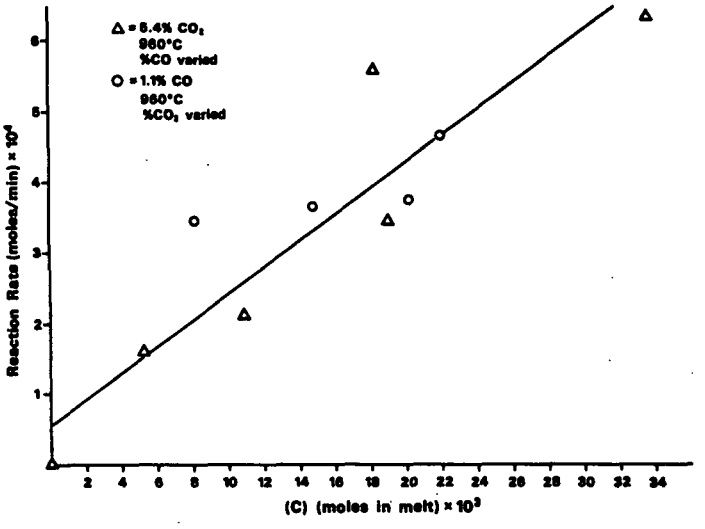

Figure 3. Effect of carbon concentration on reaction rate.

If a plot of ln(r) vs. ln[C] is made, the slope of the line is 0.65. This suggests that the rate of reaction is less than first-order in carbon concentration. This may be due to the inhibiting effect of carbon monoxide, since CO concentration increased as the carbon content was increased.

Assuming the rate-limiting step for this reaction occurs on the carbon surface and the reaction is not diffusion limited, the rate of reaction should be first order in carbon concentration. Since the effects of changes in gas concentration within the system could not be separated from the carbon effect, the method of plotting ln(r) vs ln[C] does not give an accurate result. It was assumed that the reaction rate is actually first-order in carbon concentration, and this assumption was used for the remainder of this analysis.

Temperature Effects

To determine the effect of temperature on the reaction rate, the char oxidation was studied over the temperature range of 1200-1283 K.

Figure 4 is a plot of reaction rate vs. reaction temperature, showing that the rate of reaction increases as the temperature increases. Since it was not possible to separate the CO and CO_2 effects from the temperature effects, no accurate activation energy could be graphically determined.

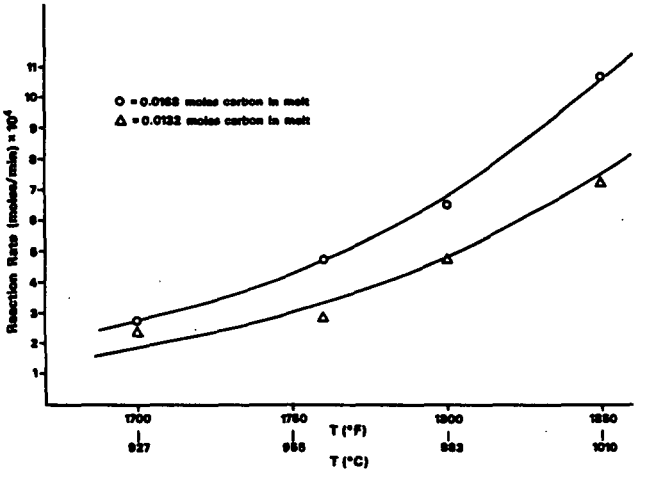

Figure 4. Effect of temperature on reaction rate.

Effect of Carbon Dioxide Partial Pressure

The effect of carbon dioxide concentration on the rate of gasification is illustrated in Figure 5. The carbon dioxide concentration varied from 1-10%. Figure 5 shows that as the concentration of carbon dioxide increases, the rate of reaction also increases. The carbon monoxide concentration could not be held constant as the carbon dioxide concentration was varied - varying one concentration automatically changed the other. The carbon monoxide concentration varied from 0.4-4.1%. It was therefore impossible to graphically determine the order of the gasification reaction with respect to carbon dioxide partial pressure.

Effect of CO Partial Pressure

The effect of carbon monoxide on the rate of reaction is shown in Figure 6. The CO concentration in the system was changed by using standard N_2, CO, CO_2 calibration gases as the reaction gas instead of using only CO_2 and a N_2 purge. The values for this plot were chosen to keep the CO_2 concentration constant at 5%. Figure 6 shows that as the percentage of carbon monoxide is increased, the rate of reaction decreases significantly. With 5% CO in the

system, the reaction rate is approximately four times slower than with 1% CO present. Therefore, the presence of carbon monoxide suppresses the gasification reaction.

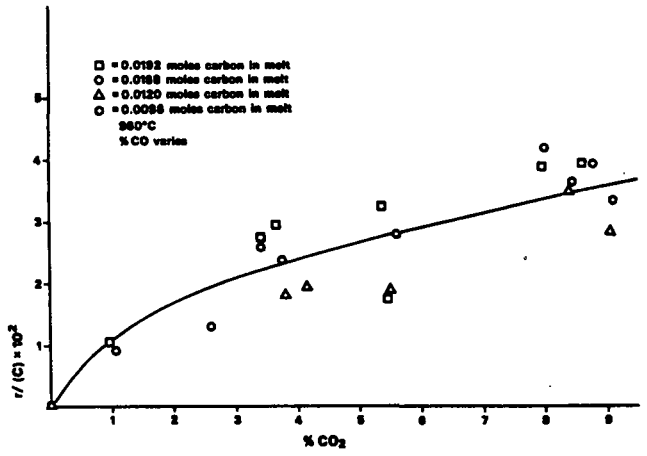

Figure 5. Effect of carbon dioxide concentration on reaction rate.

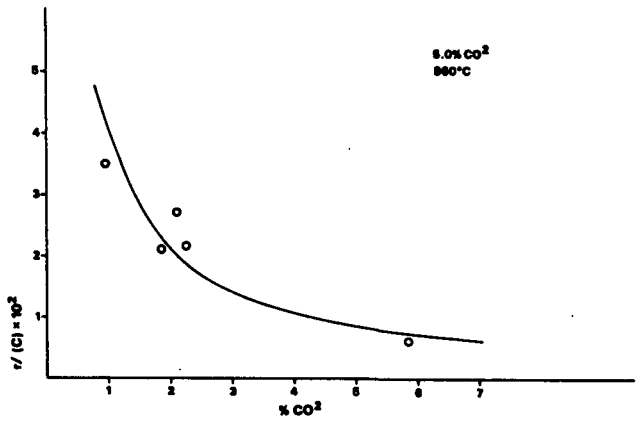

Figure 6. Effect of carbon monoxide concentration on reaction rate.

Mass Transfer Effects

In order to determine if any mass transfer limitations are present during the gasification reaction, the total gas flow rate was changed. The results from these runs were compared to the previous results and are shown in Figure 7. In this plot, the curve is the same curve as in Figure 5. The added values are from the other flow rates.

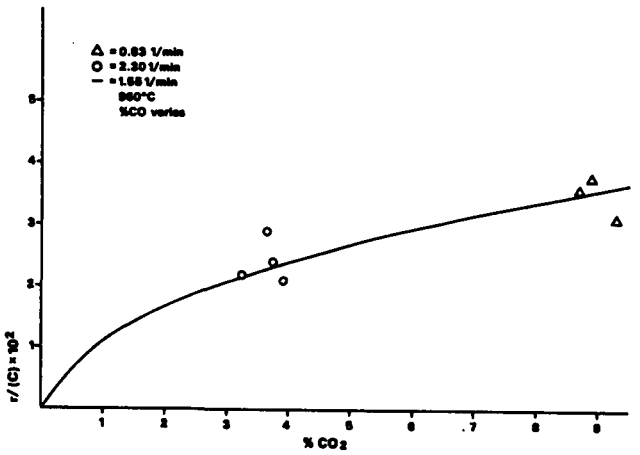

Figure 7. Effect of gas flow rate on reaction rate.

No significant difference in the gasification rate was observed. Therefore, external mass transfer limitations can be considered insignificant during the gasification reaction. The lack of flow rate effects and the high activation energy indicate that oxidation is controlled by kinetic rather than mass transfer effects.

KINETIC MODEL

The gasification reaction of the carbon content of kraft char with CO_2 is believed to occur through the adsorption of CO_2 on an active carbon site. This reaction is first-order in carbon and proportional to the CO_2 level at low CO_2 partial pressure. It is less than first order at higher CO_2 levels and is suppressed by CO. These results indicate that this reaction can be described by the following rate expression

$$\frac{d[C]}{dt} = - \frac{k_1[P_{CO_2}]\ [C]}{1 + k_2\ [P_{CO_2}] + k_3\ [P_{CO}]} e^{-\Delta E/RT} \quad (7)$$

$d[C]/dt$ is the rate of change of carbon concentration
$[C]$ is the carbon concentration
$[P_{CO_2}]$ is the partial pressure of carbon dioxide
$[P_{CO}]$ is the partial pressure of carbon monoxide
ΔE is the activation energy
T is absolute temperature
R is the gas constant
k_1, k_2, k_3 are constants

The effect of the four parameters - temperature, carbon concentration, CO_2 partial pressure, and CO partial pressure - was then determined by using a nonlinear regression analysis program (4). This program calculated the four kinetic parameters (k_1, k_2, k_3, and ΔE) found in Eq. (7). The values of these parameters are listed in Table 1.

Table 1. Parameters describing kraft char oxidation with carbon dioxide for Eq. (7).

$$\frac{d[C]}{dt} = - \frac{k_1[P_{CO_2}]\ [C]}{1 + k_2\ [P_{CO_2}] + k_3\ [P_{CO}]}\ e^{-\Delta E/RT}$$

Parameters	Value	Estimate of Standard Deviation
k_1	6.260×10^9 $(atm\ min)^{-1}$	1.823×10^9 $(atm\ min)^{-1}$
k_2	28.99 atm^{-1}	8.11 atm^{-1}
k_3	45.6 atm^{-1}	13.4 atm^{-1}
ΔE	54300 cal/mole	2250 cal/mole

The ability of this rate expression to describe the reaction is illustrated in Figure 8. Here, the model is shown by the solid line and the circles indicate the experimental data. Although this is only one data set, all other data sets show similar results.

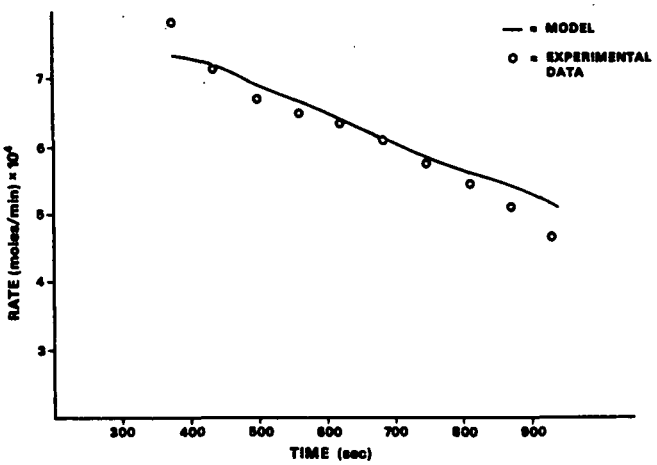

Figure 8. Comparison of kinetic model and experimental data.

This rate expression shows a good correlation with the experimental data. As the CO partial pressure increases, the experimental data indicate that the reaction rate decreases as shown in Figure 6. The data also indicate that the rate of reaction begins to level off as the CO_2 partial pressure increases. This was shown in Figure 5. At low levels of both CO and CO_2 partial pressure, the reaction rate is proportional to the CO_2 partial pressure. This rate expression agrees with the experimental results.

DISCUSSION

Carbon oxidation of kraft char was found to be dependent on carbon concentration, carbon dioxide partial pressure, and carbon monoxide partial pressure, and was found to have a high activation energy. To determine if this reaction is mass transfer or kinetically limited, the effect of different gas flow rates was studied. This was found to have no effect on the oxidation rate. This result, together with the high activation energy, indicates that the reaction is kinetically controlled rather than mass transfer controlled.

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